

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
12 September 2002 (12.09.2002)

PCT

(10) International Publication Number
WO 02/070629 A1

(51) International Patent Classification⁷: **C10G 65/12**,
65/04, 67/04

(21) International Application Number: **PCT/EP02/02366**

(22) International Filing Date: **4 March 2002 (04.03.2002)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
01400562.3 5 March 2001 (05.03.2001) EP
01402181.0 16 August 2001 (16.08.2001) EP

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (*for all designated States except US*): **SHELL INTERNATIONALE RESERACH MAATSCHAPPIJ B.V.** [NL/NL]; Carel Van Bylandtlaan 30, NL-2596 HR The Hague (NL).

Published:

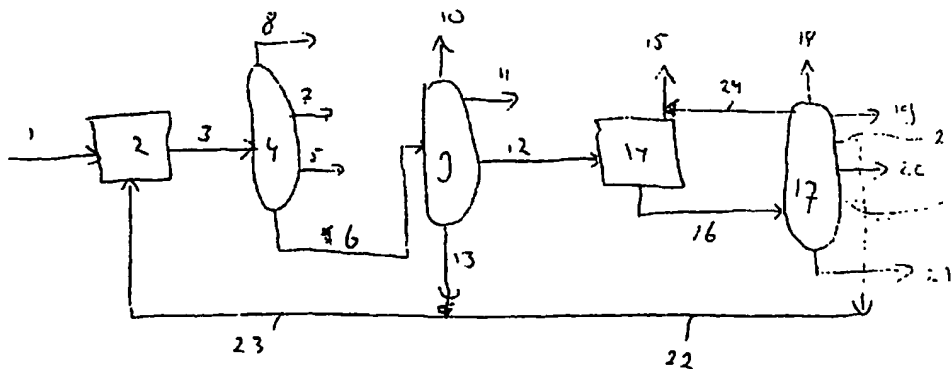
- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(72) Inventor; and

(75) Inventor/Applicant (*for US only*): **GERMAINE, Gilbert, Robert, Bernard** [FR/FR]; Route Departementale no. 3, F-76650 Petit Couronne (FR).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **PROCESS TO PREPARE A LUBRICATING BASE OIL AND A GAS OIL**



(57) Abstract: Process to prepare a lubricating base oil and a gas oil by (a) hydrocracking/hydroisomerising a Fischer-Tropsch product, wherein weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms in the Fischer-Tropsch product is at least 0.2 and wherein at least 30 wt% of compounds in the Fischer-Tropsch product have at least 30 carbon atoms, (b) separating the product of step (a) into one or more gas oil fractions, a base oil precursor fraction and a higher boiling fraction, and (c) performing a pour point reducing step to the base oil precursor fraction obtained in step (b).

PROCESS TO PREPARE A LUBRICATING BASE OIL AND A GAS OIL

The invention is directed to a process to prepare a lubricating base oil and a gas oil from a Fischer-Tropsch product.

5 Such a process is described in EP-A-776959. In the disclosed process a narrow boiling fraction of a Fischer-Tropsch wax is hydrocracked/hydroisomerised and subsequently dewaxed in order to lower the pour point. The Fischer-Tropsch wax typically has an initial boiling point of about 370 °C. The examples illustrate that a
10 base oil can be prepared having a viscosity index of 151, a pour point of -27 °C, a kinematic viscosity at 100 °C of 5 cSt and a Noack volatility of 8.8%. The yield of base oils in this experiment was 62.4% based on the Fischer-Tropsch wax. The main product of this process is
15 base oils.

 In the Fischer-Tropsch reaction a Fischer-Tropsch product is obtained comprising, next to the Fischer-Tropsch wax, a fraction boiling below 370 °C. It is furthermore desirable to prepare fuel products, such as
20 gas oils, from the Fischer-Tropsch product next to the base oil products. There is thus a desire to have a simple process, which can yield fuels products and base oils from a Fischer-Tropsch product.

 The following process provides a simple process,
25 which yields gas oils and base oils whilst minimising the number of process steps. Process to prepare a lubricating base oil and a gas oil by

 (a) hydrocracking/hydroisomerisating a Fischer-Tropsch product, wherein weight ratio of compounds having at
30 least 60 or more carbon atoms and compounds having at least 30 carbon atoms in the Fischer-Tropsch product is

at least 0.2 and wherein at least 30 wt% of compounds in the Fischer-Tropsch product have at least 30 carbon atoms,

5 (b) separating the product of step (a) into one or more gas oil fractions, a base oil precursor fraction and a higher boiling fraction, and

(c) performing a pour point reducing step to the base oil precursor fraction obtained in step (b).

10 Applicants found that by performing the hydrocracking/hydroisomerisation step with the relatively heavy feedstock a higher yield of gas oils as calculated on the feed to step (a) can be obtained. A further advantage is that both fuels, for example gas oil, and material suited for preparing base oils are prepared in
15 one hydrocracking/hydroisomerisation process step. This line up is more simple than a line up wherein a dedicated base oil hydrocracking/hydroisomerisation step is performed on a Fischer-Tropsch wax boiling mainly above 370 °C as described in for example WO-A-0014179. In a
20 preferred embodiment of the present invention all or part of the higher boiling fraction obtained in step (b) is recycled to step (a).

A further advantage is that base oils are prepared having a relatively high content of cyclo-paraffins,
25 which is favourable to achieve desired solvency properties. The content of cyclo-paraffins in the saturates fraction of the obtained base oil have been found to be between 5 and 40 wt%. Base oils having a cyclo-paraffin content in the saturates fraction of
30 between 12 and 20 wt% have been furthermore found to be excellent base stocks to formulate motor engine lubricants.

The process of the present invention also results in middle distillates having exceptionally good cold flow
35 properties. These excellent cold flow properties could

perhaps be explained by the relatively high ratio
iso/normal and especially the relatively high amount of
di- and/or trimethyl compounds. Nevertheless, the cetane
number of the diesel fraction is more than excellent at
5 values far exceeding 60, often values of 70 or more are
obtained. In addition, the sulphur content is extremely
low, always less than 50 ppmw, usually less than 5 ppmw
and in most case the sulphur content is zero. Further,
the density of especially the diesel fraction is less
10 than 800 kg/m³, in most cases a density is observed
between 765 and 790 kg/m³, usually around 780 kg/m³ (the
viscosity at 100°C for such a sample being about
3.0 cSt). Aromatic compounds are virtually absent, i.e.
less than 50 ppmw, resulting in very low particulate
15 emissions. The polyaromatic content is even much lower
than the aromatic content, usually less than 1 ppmw. T95,
in combination with the above properties, is below
380 °C, often below 350 °C.

The process as described above results in middle
20 distillates having extremely good cold flow properties.
For instance, the cloud point of any diesel fraction is
usually below -18 °C, often even lower than -24 °C. The
CFPP is usually below -20 °C, often -28 °C or lower. The
pour point is usually below -18 °C, often below -24 °C.

25 The relatively heavy Fischer-Tropsch product used in
step (a) has at least 30 wt%, preferably at least 50 wt%,
and more preferably at least 55 wt% of compounds having
at least 30 carbon atoms. Furthermore the weight ratio of
compounds having at least 60 or more carbon atoms and
30 compounds having at least 30 carbon atoms of the Fischer-
Tropsch product is at least 0.2, preferably at least 0.4
and more preferably at least 0.55. Preferably the
Fischer-Tropsch product comprises a C₂₀⁺ fraction having
an ASF-alpha value (Anderson-Schulz-Flory chain growth

factor) of at least 0.925, preferably at least 0.935, more preferably at least 0.945, even more preferably at least 0.955.

5 The initial boiling point of the Fischer-Tropsch product may range up to 400 °C, but is preferably below 200 °C. Preferably any compounds having 4 or less carbon atoms and any compounds having a boiling point in that
10 range are separated from a Fischer-Tropsch synthesis product before the Fischer-Tropsch synthesis product is used in step (a). The Fischer-Tropsch product as described in detail above is a Fischer-Tropsch product, which has not been subjected to a hydroconversion step as defined according to the present invention. The content
15 of non-branched compounds in the Fischer-Tropsch product will therefore be above 80 wt%. In addition to the Fischer-Tropsch product also other fractions may be additionally processed in step (a). Possible other
20 fractions may suitably be the higher boiling fraction obtained in step (b) or part of said fraction and/or off-spec base oil fractions as obtained in step (c).

 Such a Fischer-Tropsch product can be obtained by any process, which yields a relatively heavy Fischer-Tropsch product. Not all Fischer-Tropsch processes yield such a heavy product. An example of a suitable Fischer-Tropsch
25 process is described in WO-A-9934917 and in AU-A-698392. These processes may yield a Fischer-Tropsch product as described above.

 The Fischer-Tropsch product will contain no or very little sulphur and nitrogen containing compounds. This is
30 typical for a product derived from a Fischer-Tropsch reaction, which uses synthesis gas containing almost no impurities. Sulphur and nitrogen levels will generally be below the detection limits, which are currently 5 ppm for sulphur and 1 ppm for nitrogen.

The Fischer-Tropsch product may optionally be subjected to a mild hydrotreatment step in order to remove any oxygenates and saturate any olefinic compounds present in the reaction product of the Fischer-Tropsch reaction. Such a hydrotreatment is described in EP-B-668342. The mildness of the hydrotreating step is preferably expressed in that the degree of conversion in this step is less than 20 wt% and more preferably less than 10 wt%. The conversion is here defined as the weight percentage of the feed boiling above 370 °C, which reacts to a fraction boiling below 370 °C. After such a mild hydrotreatment lower boiling compounds, having four or less carbon atoms and other compounds boiling in that range, will preferably be removed from the effluent before it is used in step (a).

The hydrocracking/hydroisomerisation reaction of step (a) is preferably performed in the presence of hydrogen and a catalyst, which catalyst can be chosen from those known to one skilled in the art as being suitable for this reaction. Catalysts for use in step (a) typically comprise an acidic functionality and a hydrogenation/dehydrogenation functionality. Preferred acidic functionality's are refractory metal oxide carriers. Suitable carrier materials include silica, alumina, silica-alumina, zirconia, titania and mixtures thereof. Preferred carrier materials for inclusion in the catalyst for use in the process of this invention are silica, alumina and silica-alumina. A particularly preferred catalyst comprises platinum supported on a silica-alumina carrier. If desired, applying a halogen moiety, in particular fluorine, or a phosphorous moiety to the carrier, may enhance the acidity of the catalyst carrier. Examples of suitable hydrocracking/hydroisomerisation processes and suitable catalysts are

described in WO-A-0014179, EP-A-532118, EP-A-666894 and the earlier referred to EP-A-776959.

Preferred hydrogenation/dehydrogenation functionality's are Group VIII noble metals, for example palladium and more preferably platinum. The catalyst may comprise the hydrogenation/dehydrogenation active component in an amount of from 0.005 to 5 parts by weight, preferably from 0.02 to 2 parts by weight, per 100 parts by weight of carrier material. A particularly preferred catalyst for use in the hydroconversion stage comprises platinum in an amount in the range of from 0.05 to 2 parts by weight, more preferably from 0.1 to 1 parts by weight, per 100 parts by weight of carrier material. The catalyst may also comprise a binder to enhance the strength of the catalyst. The binder can be non-acidic. Examples are clays and other binders known to one skilled in the art.

In step (a) the feed is contacted with hydrogen in the presence of the catalyst at elevated temperature and pressure. The temperatures typically will be in the range of from 175 to 380 °C, preferably higher than 250 °C and more preferably from 300 to 370 °C. The pressure will typically be in the range of from 10 to 250 bar and preferably between 20 and 80 bar. Hydrogen may be supplied at a gas hourly space velocity of from 100 to 10000 Nl/l/hr, preferably from 500 to 5000 Nl/l/hr. The hydrocarbon feed may be provided at a weight hourly space velocity of from 0.1 to 5 kg/l/hr, preferably higher than 0.5 kg/l/hr and more preferably lower than 2 kg/l/hr. The ratio of hydrogen to hydrocarbon feed may range from 100 to 5000 Nl/kg and is preferably from 250 to 2500 Nl/kg.

The conversion in step (a) as defined as the weight percentage of the feed boiling above 370 °C which reacts per pass to a fraction boiling below 370 °C, is at least 20 wt%, preferably at least 25 wt%, but preferably not

more than 80 wt%, more preferably not more than 70 wt%.
The feed as used above in the definition is the total
hydrocarbon feed fed to step (a), thus also any optional
recycle of the higher boiling fraction as obtained in
step (b).

In step (b) the product of step (a) is separated into
one or more gas oil fractions, a base oil precursor
fraction having preferably a T10 wt% boiling point of
between 200 and 450 °C and a T90 wt% boiling point of
between 300, and preferably between 400 and 550 °C and a
higher boiling fraction. By performing step (c) on the
preferred narrow boiling base oil precursor fraction
obtained in step (b) a haze free base oil grade can be
obtained having also excellent other quality properties.
The separation is preferably performed by means of a
first distillation at about atmospheric conditions,
preferably at a pressure of between 1.2-2 bara, wherein
the gas oil product and lower boiling fractions, such as
naphtha and kerosine fractions, are separated from the
higher boiling fraction of the product of step (a). The
higher boiling fraction, of which suitably at least
95 wt% boils above 370 °C, is subsequently further
separated in a vacuum distillation step wherein a vacuum
gas oil fraction, the base oil precursor fraction and the
higher boiling fraction are obtained. The vacuum
distillation is suitably performed at a pressure of
between 0.001 and 0.05 bara.

The base oil precursor fraction may in addition or
alternatively be a fraction boiling in the gas oil range
as obtained in the atmospheric distillation step. It has
been found that from such a fraction a base oil having a
kinematic viscosity at 100 °C of between about 2 and
about 3 cSt can be obtained, especially when the pour
point reducing step (c) is performed by a catalytic
dewaxing process as described below in more detail.

The vacuum distillation of step (b) is preferably operated such that the desired base oil precursor fraction is obtained boiling in the specified range and having a kinematic viscosity, which relates to the base oil end product(s) specification. The kinematic viscosity at 100 °C of the base oil precursor fraction is preferably between 3 and 10 cSt.

In a first embodiment of the present invention one base oil grade is prepared at a time from the base oil precursor fraction. If, for example, in this embodiment two or more base oil grades are to be prepared having different kinematic viscosities at 100 °C step (b) is suitably performed as follows. The separate base oil grades are prepared in a blocked out mode from base oil precursor fractions which properties correspond with the desired base oil grades. The base oil precursor fraction is prepared one after the other in a period of time in the vacuum distillation. It has been found that by performing the vacuum distillation sequentially for each desired base oil grade high yields of the separate base oils can be obtained. This is especially the case when the difference in kinematic viscosity at 100 °C between the various grades is small, i.e. smaller than 2 cSt. In this manner a base oil grade having a kinematic viscosity at 100 °C of between 3.5 and 4.5 cSt and a second base oil grade having a kinematic viscosity at 100 °C of between 4.5 and 5.5 cSt can be advantageously prepared in high yields by performing the vacuum distillation in a first mode (v1) to obtain a base oil precursor fraction having a kinematic viscosity at 100 °C corresponding to the first base oil grade and in a second mode (v2) to obtain a base oil precursor fraction having a kinematic viscosity at 100 °C corresponding to the second base oil grade. By performing the pour point reducing step (c)

separately on the first and second base oil precursor fractions high quality base oils can be obtained.

After performing a catalytic dewaxing step (c) or after the optional hydrogenation step (d) (see below)

5 lower boiling compounds formed during catalytic dewaxing are removed, preferably by means of distillation, optionally in combination with an initial flashing step. By choosing a suitable distillation cut in the alternating vacuum distillation mode (v) of step (b) it

10 is possible to obtain the separate base oil directly after a catalytic dewaxing step (c) or optional step (d) without having to remove any higher boiling compounds from the end base oil grade. In a preferred embodiment a first base oil (grade-4) is prepared having a kinematic

15 viscosity at 100 °C of between 3.5 and 4.5 cSt (according to ASTM D 445), a Noack volatility of below 20 wt%, preferably below 14 wt% (according to CEC L40 T87) and a pour point of between -15 and -60 °C, preferably between -25 and -60 °C, (according to ASTM D 97) by catalytic

20 dewaxing in step (b) a distillate fraction obtained in step (a) having a kinematic viscosity at 100 °C of between 3.2 and 4.4 cSt and a second base oil (grade-5) is prepared having a kinematic viscosity at 100 °C of between 4.5 and 5.5, a Noack volatility of lower than

25 14 wt% preferably lower than 10 wt% and a pour point of between -15 and -60 °C, preferably between -25 and -60 °C, by catalytic dewaxing in step (b) a distillate fraction obtained in step (a) having a kinematic viscosity at 100 °C ($\nu K@100$) of between 4.2 and 5.4 cSt.

30 In a second embodiment of the present invention more than one viscosity grade base oil is prepared at a time starting from a base oil precursor fraction. In this mode the effluent of step (c) or the optional step (d) is separated into various distillate fractions comprising

two or more base oil grades. In order to meet the desired viscosity grades and volatility requirements of the various base oil grades preferably off-spec fractions boiling between, above and/or below the desired base oil grades are also obtained as separate fractions. These fractions having an initial boiling point of above 340 °C may advantageously be recycled to step (a). Any fractions obtained boiling in the gas oil range or below may suitably be recycled to step (b) or alternatively be used as a blending component to prepare a gas oil fuel composition. The separation into the various fractions may suitably be performed in a vacuum distillation column provided with side strippers to separate the fraction from said column. In this mode it is found possible to obtain for example a base oil having a viscosity between 2-3 cSt, a base oil having a viscosity between 4-6 cSt and a base oil having a viscosity between 7-10 cSt product simultaneously from a single base oil precursor fraction (viscosities as kinematic viscosity at 100 °C). A grade-4 and/or grade-5 base oil having the properties as described above may advantageously be obtained as the 4-6 cSt base oil product.

In step (c) the base oil precursor fraction obtained in step (b) is subjected to a pour point reducing treatment. With a pour point reducing treatment is understood every process wherein the pour point of the base oil is reduced by more than 10 °C, preferably more than 20 °C, more preferably more than 25 °C.

The pour point reducing treatment can be performed by means of a so-called solvent dewaxing process or by means of a catalytic dewaxing process. Solvent dewaxing is well known to those skilled in the art and involves admixture of one or more solvents and/or wax precipitating agents with the base oil precursor fraction and cooling the

mixture to a temperature in the range of from -10 °C to -40 °C, preferably in the range of from -20 °C to -35 °C, to separate the wax from the oil. The oil containing the wax is usually filtered through a filter cloth which can
5 be made of textile fibres, such as cotton; porous metal cloth; or cloth made of synthetic materials. Examples of solvents which may be employed in the solvent dewaxing process are C₃-C₆ ketones (e.g. methyl ethyl ketone, methyl isobutyl ketone and mixtures thereof), C₆-C₁₀
10 aromatic hydrocarbons (e.g. toluene), mixtures of ketones and aromatics (e.g. methyl ethyl ketone and toluene), autorefrigerative solvents such as liquefied, normally gaseous C₂-C₄ hydrocarbons such as propane, propylene, butane, butylene and mixtures thereof. Mixtures of methyl
15 ethyl ketone and toluene or methyl ethyl ketone and methyl isobutyl ketone are generally preferred. Examples of these and other suitable solvent dewaxing processes are described in Lubricant Base Oil and Wax Processing, Avilino Sequeira, Jr, Marcel Dekker Inc., New York, 1994,
20 Chapter 7.

Preferably step (c) is performed by means of a catalytic dewaxing process. With such a process it has been found that base oils having a pour point of even below -40 °C can be prepared when starting from a base
25 oil precursor fraction as obtained in step (b) of the present process.

The catalytic dewaxing process can be performed by any process wherein in the presence of a catalyst and hydrogen the pour point of the base oil precursor
30 fraction is reduced as specified above. Suitable dewaxing catalysts are heterogeneous catalysts comprising a molecular sieve and optionally in combination with a metal having a hydrogenation function, such as the Group VIII metals. Molecular sieves, and more suitably

intermediate pore size zeolites, have shown a good catalytic ability to reduce the pour point of the base oil precursor fraction under catalytic dewaxing conditions. Preferably the intermediate pore size zeolites have a pore diameter of between 0.35 and 0.8 nm. Suitable intermediate pore size zeolites are mordenite, ZSM-5, ZSM-12, ZSM-22, ZSM-23, SSZ-32, ZSM-35 and ZSM-48. Another preferred group of molecular sieves are the silica-aluminaphosphate (SAPO) materials of which SAPO-11 is most preferred as for example described in US-A-4859311. ZSM-5 may optionally be used in its HZSM-5 form in the absence of any Group VIII metal. The other molecular sieves are preferably used in combination with an added Group VIII metal. Suitable Group VIII metals are nickel, cobalt, platinum and palladium. Examples of possible combinations are Pt/ZSM-35, Ni/ZSM-5, Pt/ZSM-23, Pd/ZSM-23, Pt/ZSM-48 and Pt/SAPO-11. Further details and examples of suitable molecular sieves and dewaxing conditions are for example described in WO-A-9718278, US-A-4343692, US-A-5053373, US-A-5252527 and US-A-4574043.

The dewaxing catalyst suitably also comprises a binder. The binder can be a synthetic or naturally occurring (inorganic) substance, for example clay, silica and/or metal oxides. Natural occurring clays are for example of the montmorillonite and kaolin families. The binder is preferably a porous binder material, for example a refractory oxide of which examples are: alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions for example silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. More preferably a low acidity refractory oxide binder material, which is essentially free of alumina, is used. Examples of these

binder materials are silica, zirconia, titanium dioxide, germanium dioxide, boria and mixtures of two or more of these of which examples are listed above. The most preferred binder is silica.

5 A preferred class of dewaxing catalysts comprise intermediate zeolite crystallites as described above and a low acidity refractory oxide binder material which is essentially free of alumina as described above, wherein the surface of the aluminosilicate zeolite crystallites
10 has been modified by subjecting the aluminosilicate zeolite crystallites to a surface dealumination treatment. A preferred dealumination treatment is by contacting an extrudate of the binder and the zeolite with an aqueous solution of a fluorosilicate salt as
15 described in for example US-A-5157191 or WO-A-0029511. Examples of suitable dewaxing catalysts as described above are silica bound and dealuminated Pt/ZSM-5, silica bound and dealuminated Pt/ZSM-23, silica bound and dealuminated Pt/ZSM-12, silica bound and dealuminated
20 Pt/ZSM-22, as for example described in WO-A-0029511 and EP-B-832171.

Catalytic dewaxing conditions are known in the art and typically involve operating temperatures in the range of from 200 to 500 °C, suitably from 250 to 400 °C,
25 hydrogen pressures in the range of from 10 to 200 bar, preferably from 40 to 70 bar, weight hourly space velocities (WHSV) in the range of from 0.1 to 10 kg of oil per litre of catalyst per hour (kg/l/hr), suitably from 0.2 to 5 kg/l/hr, more suitably from 0.5 to
30 3 kg/l/hr and hydrogen to oil ratios in the range of from 100 to 2,000 litres of hydrogen per litre of oil. By varying the temperature between 275, suitably between 315 and 375 °C at between 40-70 bars, in the catalytic dewaxing step it is possible to prepare base oils having

different pour point specifications varying from suitably -10 to -60 °C.

5 The effluent of step (c) is optionally subjected to an additional hydrogenation step (d), also referred to as a hydrofinishing step for example if the effluent contains olefins or when the product is sensitive to oxygenation. This step is suitably carried out at a temperature between 180 and 380 °C, a total pressure of between 10 to 250 bar and preferably above 100 bar and
10 more preferably between 120 and 250 bar. The WHSV (Weight hourly space velocity) ranges from 0.3 to 2 kg of oil per litre of catalyst per hour (kg/l.h).

The hydrogenation catalyst is suitably a supported catalyst comprising a dispersed Group VIII metal.
15 Possible Group VIII metals are cobalt, nickel, palladium and platinum. Cobalt and nickel containing catalysts may also comprise a Group VIB metal, suitably molybdenum and tungsten. Suitable carrier or support materials are low acidity amorphous refractory oxides. Examples of suitable
20 amorphous refractory oxides include inorganic oxides, such as alumina, silica, titania, zirconia, boria, silica-alumina, fluorided alumina, fluorided silica-alumina and mixtures of two or more of these.

Examples of suitable hydrogenation catalysts are
25 nickel-molybdenum containing catalyst such as KF-847 and KF-8010 (AKZO Nobel) M-8-24 and M-8-25 (BASF), and C-424, DN-190, HDS-3 and HDS-4 (Criterion); nickel-tungsten containing catalysts such as NI-4342 and NI-4352 (Engelhard) and C-454 (Criterion); cobalt-molybdenum
30 containing catalysts such as KF-330 (AKZO-Nobel), HDS-22 (Criterion) and HPC-601 (Engelhard). Preferably platinum containing and more preferably platinum and palladium containing catalysts are used. Preferred supports for these palladium and/or platinum containing catalysts are
35 amorphous silica-alumina. Examples of suitable silica-

alumina carriers are disclosed in WO-A-9410263. A preferred catalyst comprises an alloy of palladium and platinum preferably supported on an amorphous silica-alumina carrier of which the commercially available catalyst C-624 of Criterion Catalyst Company (Houston, TX) is an example.

Figure 1 shows a preferred embodiment of the process according to the present invention. To a hydrocracker reactor (2) a Fischer-Tropsch product (1) is fed. After separation of gaseous products the effluent (3) is separated into a naphtha fraction (8), a kerosene fraction (7), a gas oil fraction (5) and a residue (6). Residue (6) is subsequently further separated in a vacuum distillation column (9) into tops (10), a vacuum gas oil fraction (11), a base oil precursor fraction (12) and a higher boiling fraction (13). The higher boiling fraction (13) is recycled via (23) to reactor (2). The base oil precursor fraction is used a feed to a catalytic dewaxing reactor (14), usually a packed bed reactor.

An intermediate product (16) is obtained by separating the gaseous fraction and part of the gas oil fraction and those compounds boiling within that range (15), which are formed during the catalytic dewaxing process, from the effluent of reactor (14). Intermediate product (16) is fed to a vacuum distillation column (17), which column (17) is provided with means, e.g. side strippers, to discharge along the length of the tower different fractions boiling between the top and bottom distillation products. In Figure 1 tops (18), a gas oil fraction (24), a light base oil grade (19), an intermediate base oil grade (20) and a heavy base oil grade (21) are obtained as distillate products of column (17). In order to meet volatility requirements of grades (20) and (21) intermediate fractions (22) are withdrawn from the column and recycled via (23) to

hydrocracker (2). Gas oil fractions obtained as (24) and (15) may be recycled to distillation column (4) (not shown). Alternatively it may also be possible that the bottom distillate product of column (17) cannot be used as a base oil grade. In such a situation the bottom distillate product is suitably recycled to reactor (2) (not shown).

The above-described Base oil grade-4 can suitably find use as base oil for an Automatic Transmission Fluids (ATF). If the desired $\nu K@100$ of the ATF is between 3 and 3.5 cSt, the Base Oil grade-4 is suitably blended with a grade having a $\nu K@100$ of about 2 cSt. The base oil having a kinematic viscosity at 100 °C of about 2 to 3 cSt can suitably be obtained by catalytic dewaxing of a suitable gas oil fraction as obtained in the atmospheric and/or vacuum distillation in step (b) as described above. The Automatic Transmission Fluid will comprise the base oil as described above, preferably having a $\nu K@100$ of between 3 and 6 cSt, and one or more performance additives. Examples of such performance additives are an antiwear agent, an antioxidant, an ashless dispersant, a pour point depressant, and antifoam agent, a friction modifier, a corrosion inhibitor and a viscosity modifier.

The base oils obtained by the present process having intermediate $\nu K@100$ values of between 2 and 9 cSt, of which preferred grades have been described above, are preferably used as base oil in formulations such as automotive (gasoline or diesel) engine oils, electrical oils or transformer oils and refrigerator oils. The use in electrical and refrigerator oils is advantageous because of the naturally low pour point when such a base oil, especially the grades having a pour point of below -40 °C, is used to blend such a formulation. This is advantageous because the highly iso-paraffinic base oil has a naturally high resistance to oxidation compared to

low pour point naphthenic type base oils. Especially the base oils having the very low pour points, suitably lower than -40°C , have been found to be very suitable for use in lubricant formulations such as automotive engine oils of the 0W-xx specification according to the SAE J-300 viscosity classification, wherein xx is 20, 30, 40, 50 or 60. It has been found that these high tier lubricant formulations can be prepared with the base oils obtainable by the process of the current invention. Other possible engine oil applications are the 5W-xx and the 10W-xx formulations, wherein the xx is as above. The engine oil formulation will suitably comprise the above described base oil and one or more of additives. Examples of additive types which may form part of the composition are ashless dispersants, detergents, preferably of the over-based type, viscosity modifying polymers, extreme pressure/antiwear additives, preferably of the zinc dialkyl dithiophosphate type (ZDTP), antioxidants, preferably of the hindered phenolic or aminic type, pour point depressants, emulsifiers, demulsifiers, corrosion inhibitors, rust inhibitors, antistaining additives and/or friction modifiers. Specific examples of such additives are described in for example Kirk-Othmer Encyclopedia of Chemical Technology, third edition, volume 14, pages 477-526.

The invention will be illustrated with the following non-limiting examples.

Example 1

The $\text{C}_5\text{-C}_{750}^{\circ}\text{C}^+$ fraction of the Fischer-Tropsch product, as obtained in Example VII using the catalyst of Example III of WO-A-9934917 was continuously fed to a hydrocracking step (step (a)). The feed contained about 60 wt% C_{30}^+ product. The ratio $\text{C}_{60}^+/\text{C}_{30}^+$ was about 0.55.

In the hydrocracking step the fraction was contacted with a hydrocracking catalyst of Example 1 of EP-A-532118.

5 The effluent of step (a) was continuously distilled to give lights, fuels and a residue "R" boiling from 370 °C and above. The yield of gas oil fraction on fresh feed to hydrocracking step was 43 wt%. The main part of the residue "R" was recycled to step (a) and a remaining part was separated by means of a vacuum distillation into a base oil precursor fraction having the properties as in
10 Table 1 and a fraction boiling above 510 °C.

The conditions in the hydrocracking step (a) were: a fresh feed Weight Hourly Space Velocity (WHSV) of 0.8 kg/l.h, recycle feed WHSV of 0.2 kg/l.h, hydrogen gas rate = 1000 Nl/kg, total pressure = 40 bar, and a reactor
15 temperature of 335 °C.

Table 1

Density at 70°C (kg/m ³)	779.2
vK@100 (cSt)	3.818
pour point (°C)	+18
Boiling point data as temperature at which a wt% is recovered.	5% 355 °C 10% 370 °C 50% 419 °C 90% 492 °C 95% 504 °C

In the dewaxing step, the fraction of Table 1 was contacted with a dealuminated silica bound ZSM-5 catalyst comprising 0.7% by weight Pt and 30 wt% ZSM-5 as described in Example 9 of WO-A-0029511. The dewaxing
20 conditions were 40 bar hydrogen, WHSV = 1 kg/l.h and a temperature of 340 °C.

5 The dewaxed oil was distilled into three base oil fractions: boiling between 378 and 424 °C (yield based on feed to dewaxing step was 14.2 wt%), between 418-455 °C (yield based on feed to dewaxing step was 16.3 wt%) and a fraction boiling above 455 °C (yield based on feed to dewaxing step was 21.6 wt%). See Table 2 for more details.

Table 2

	Light Grade	Medium Grade	Heavy Grade
density at 20 °C	805.8	814.6	822.4
pour point (°C)	< -63	< -51	- 45
kinematic viscosity at 40 °C (cSt)		19.06	35.0
kinematic viscosity at 100 °C (cSt)	3.16	4.144	6.347
VI	n.a.	121	134
Noack volatility (wt%)	n.a.	10.8	2.24
sulphur content (ppm)	< 1 ppm	< 1 ppm	< 5 ppm
saturates (%w)	n.a.	99.9	n.a.
Content of cyclo- paraffins (wt%) (*)	n.a.	18.5	n.a.
Dynamic viscosity as measured by CCS at -40 °C	n.a.	3900 cP	n.a.

(*) as determined by means of a Finnigan MAT90 mass spectrometer equipped with a Field desorption/field ionisation interface on the saturates fraction of said base oil.

n.a.: not applicable

n.d.: not determined

Example 2

Example 1 was repeated except that the dewaxed oil was distilled into the different three base oil products of which the properties are presented in Table 3.

Table 3

	Light Grade	Medium Grade	Heavy Grade
density at 20 °C	809.1	817.2	825.1
pour point (°C)	< -63	< -51	- 39
kinematic viscosity at 40 °C (cSt)		23.32	43.01
kinematic viscosity at 100 °C (cSt)	3.181	4.778	7.349
VI	n.a.	128	135
Noack volatility (wt%)	n.a.	7.7	n.a.
sulphur content (ppm)	< 5 ppm	< 5 ppm	< 5 ppm
saturates (%w)		99.0	
Dynamic viscosity as measured by CCS at -40 °C		5500 cP	
Yield based on feed to cat dewaxing step (wt%)	15.3	27.4	8.9

5

Example 3

Example 1 was repeated except that the that the dewaxed oil was distilled into the different three base oil products and one intermediate raffinate (I.R.) of which the properties are presented in Table 4.

Table 4

	Light Grade	I.R.	Medium Grade	Heavy Grade
density at 20 °C	806	811.3	817.5	824.5
pour point (°C)	< -63	-57	< -51	- 39
Kinematic viscosity at 40 °C (cSt)	10.4		23.51	42.23
Kinematic viscosity at 100 °C (cSt)	2.746	3.501	4.79	7.24
VI	103		127	135
Noack volatility	n.a.		6.8	1.14
sulphur content (ppm)	< 5 ppm		< 5 ppm	< 5 ppm
Saturates (%w)	n.d.		99.5	
Dynamic viscosity as measured by CCS at -40 °C			5500 cP	
Yield based on CDW feed	22.6	8.9	22.6	11.1

n.a.: not applicable

n.d.: not determined

Example 4

74.6 weight parts of a base oil, having the properties as listed in Table 5 and which was obtained by catalytic dewaxing of a hydroisomerised/hydrocracked Fischer-Tropsch product using the same feed and procedure as illustrated by Examples 1-3, was blended with 14.6 weight parts of a standard detergent inhibitor additive package, 0.25 weight parts of a corrosion inhibitor and 10.56 weight parts of a viscosity modifier. The properties of the resulting composition are listed in Table 6. Table 6 also shows the 0W-30 specifications for motor gasoline lubricants. It is clear that the

composition as obtained in this Example meets the requirements of an 0W30 motor gasoline specification..

Comparative experiment A

5 54.65 weight parts of a poly-alpha olefin-4 (PAO-4) and 19.94 weight parts of a poly-alpha olefin-5 (PAO-5), having the properties as listed in Table 5 were blended with the same quantity and quality of additives as in Example 3. The properties of the resulting composition are listed in Table 6.

10 This experiment and Example 4 shows that a base oil as obtained by the present invention can be successfully used to formulate 0W-30 motor gasoline lubricants using the same additives as used to formulate such a grade based on poly-alpha olefins.

Table 5

	PAO-4	PAO-5	Base oil of Example 4
kinematic viscosity at 100 °C (1)	3.934	5.149	4.234
kinematic viscosity at 40 °C (2)	17.53	24.31	19.35
viscosity index (3)	121	148	125
VDCCS@ -35 °C (P) (4)	13.63	23.08	21.17
VDCCS@ -30 °C (P) (5)	10.3	16	14.1
MRV cP @ -40 °C (6)	2350	4070	3786
Pour Point °C (7)	Less than -66	-45	-45
Noack (wt%) (8)	13.4	6.6	10.6
Content(**) cyclo- paraffins (wt%)	n.a. (*)	n.a.	14 wt%

(*) Not analysed but presumed to be zero due to the manner in which poly-alpha olefins are prepared.

(**) Content as based on the whole base oil composition

(1) Kinematic viscosity at 100 °C as determined by ASTM D 445, (2) Kinematic viscosity at 40 °C as determined by ASTM D 445, (3) Viscosity Index as determined by ASTM D 2270, (4) VDCCS@ -35 °C (P) stands for dynamic viscosity at -35 degrees Centigrade and is measured according to ASTM D 5293, (5) VDCCS@ -35 °C (P) stands for dynamic viscosity at -35 degrees Centigrade and is measured according to ASTM D 5293, (6) MRV cP @ -40 °C stands for mini rotary viscometer test and is measured according to ASTM D 4684, (7) pour point according to ASTM D 97, (8) Noack volatility as determined by ASTM D 5800 (Tables 1-6).

Table 6

	0W-30 specifi- cations	Example 4	Comparative experiment A
kinematic viscosity at 100 °C (cSt)	9.3-12.5	9.69	9.77
VDCCS P @ -35 °C (cP)	62.0 max	61.2	48.3
MRV cP @ -40 °C (cP)	60000 max	17500	12900
Yield stress	No	No	No
Pour Point (°C)	-	-60	-60
Noack (wt%)	-	11.7	11.2

C L A I M S

1. 1. Process to prepare a lubricating base oil and a gas oil by
 - (a) hydrocracking/hydroisomerisating a Fischer-Tropsch product, wherein weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms in the Fischer-Tropsch product is at least 0.2 and wherein at least 30 wt% of compounds in the Fischer-Tropsch product have at least 30 carbon atoms,
 - (b) separating the product of step (a) into one or more gas oil fractions, a base oil precursor fraction and a higher boiling fraction, and
 - (c) performing a pour point reducing step to the base oil precursor fraction obtained in step (b).
2. Process according to claim 1, wherein at least 50 wt% of compounds in the Fischer-Tropsch product have at least 30 carbon atoms.
3. Process according to any one of claims 1-2, wherein the weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms in the Fischer-Tropsch product is at least 0.4.
4. Process according to any one of claims 1-3, wherein the conversion in step (a) is between 25 and 70 wt%.
5. Process according to any one of claims 1-4, wherein the base oil precursor fraction has a T10 wt% boiling point of between 200 and 450 °C and a T90 wt% boiling point of between 400 and 550 °C.
6. Process according to claim 5, wherein the base oil precursor fraction has a kinematic viscosity at 100 °C of between 3 and 10 cSt.

7. Process according to any one of claims 1-6, wherein two or more base oil grades are prepared from two or more corresponding base oil precursor fractions, which base oil grades have a difference in kinematic viscosity at 100 °C of less than 2 cSt and wherein step (b) is performed such that each base oil precursor fraction is prepared one after the other in a period of time.
8. Process according to any one of claims 1-7, wherein the base oil having the desired specifications is the directly obtained product of step (c) from which only a lower boiling fraction is removed.
9. Process according to any one of claims 1-8, wherein a base oil is prepared having a kinematic viscosity at 100 °C of between 3.5 and 4.5, a Noack volatility lower than 14%w and a pour point of between -15 and -60 °C by catalytic dewaxing in step (c) a base oil precursor fraction obtained in step (b) having a kinematic viscosity at 100 °C of between 3.2 and 4.4 cSt.
10. Process according to any one of claims 1-8, wherein a base oil is prepared having a kinematic viscosity at 100 °C of between 4.5 and 5.5, a Noack volatility lower than 10 wt% and a pour point of between -15 and -60 °C by catalytic dewaxing in step (c) a base oil precursor fraction obtained in step (b) having a kinematic viscosity at 100 °C of between 4.2 and 5.4 cSt.
11. Process according to any one of claims 1-6, wherein the dewaxed fraction obtained in step (c) is separated into two or more base oil grades by means of a vacuum distillation step and wherein the required volatility properties of the base oil grades are met by also separating a fraction boiling just below at least one of said grades.
12. Process according to claim 11, wherein the fractions boiling just below the base oil grades and having an

initial boiling point of above 340 °C are recycled to step (a).

5 13. Process according to any one of claims 11-12, wherein the vacuum distillation step is performed in a vacuum distillation column provided with side strippers.

14. Process according to any one of claims 1-13, wherein part or all of the higher boiling fraction obtained in step (b) is recycled to step (a).

10 15. Process according to any one of claims 1-14, wherein step (c) is performed by means of solvent dewaxing.

16. Process according to any one of claims 1-14, wherein step (c) is performed by means of catalytic dewaxing.

15 17. Process according to claim 16, wherein the catalytic dewaxing is performed in the presence of a catalyst comprising a Group VIII metal, an intermediate pore size zeolite having pore diameter between 0.35 and 0.8 nm, and a low acidity refractory binder which binder is essentially free of alumina.

20 18. Automotive engine oil comprising the base oil obtained by the process according to claims 9 or 10.

19. Automotive engine oil according to claim 18 according to the 0W-xx specification according to SAE J-300 viscosity classification.

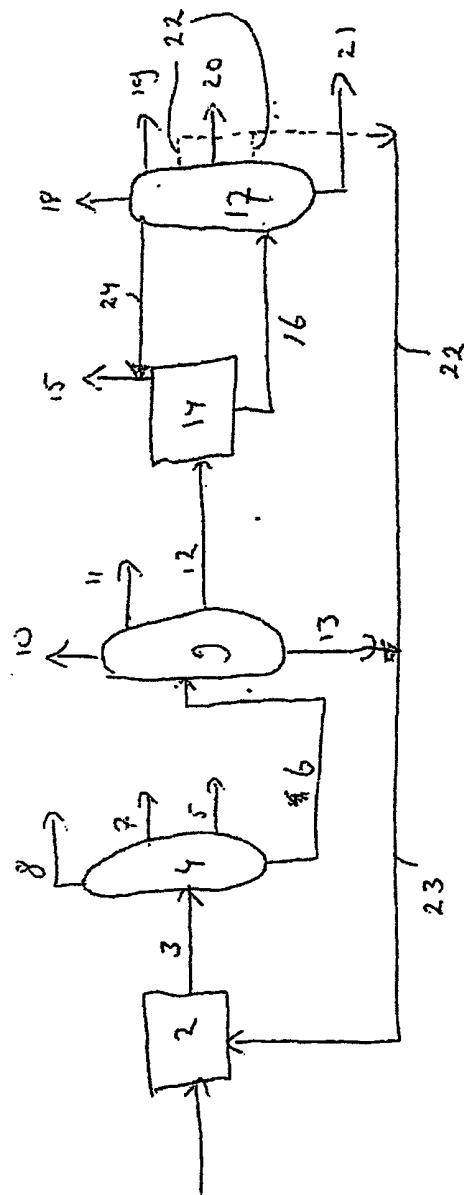


Fig.1

International Application No.
PCT/EP 02/02366

IPC 7 C10G65/12 C10G65/04 C10G67/04

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10G

EPO-Internal, WPI Data, PAJ

X	WO 96 03359 A (MOBIL OIL CORP) 8 February 1996 (1996-02-08) claim 1 page 10, line 11 - line 13 page 10, line 18 - line 22 page 11, line 13 - line 17 table 1 example 1 abstract	1,2,4,6, 15,16
X	WO 00 15736 A (EXXON RESEARCH ENGINEERING CO) 23 March 2000 (2000-03-23) the whole document	1-10, 14-17
X	US 6 165 949 A (HABEEB JACOB J ET AL) 26 December 2000 (2000-12-26) claims 1-28	1-10, 14-17

☒ Patent family members are listed in annex.

'&' document member of the same patent family

29/07/2002

De Herdt, O

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/02366

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 21788 A (EXXON RESEARCH ENGINEERING CO) 19 June 1997 (1997-06-19) claims 1,2,8 page 4, paragraph 1 table 1	1,4,8
A	US 6 179 994 B1 (CLARK JANET R ET AL) 30 January 2001 (2001-01-30) claims 1-3,5,11 column 6, line 34 - line 39 column 8, line 33 - line 35	1,4
A	EP 0 776 959 A (SHELL INT RESEARCH) 4 June 1997 (1997-06-04) cited in the application the whole document	1-10, 14-17
P,A	WO 01 18156 A (TOTAL RAFFINAGE DISTRIB S A ;BERTOMEU OLIVIER (FR)) 15 March 2001 (2001-03-15)	
A	WO 99 20720 A (MOBIL OIL CORP) 29 April 1999 (1999-04-29)	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/02366

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9603359	A	08-02-1996	US 5362378 A WO 9603359 A1 AU 695832 B2 AU 7474494 A DE 69421100 D1 DE 69421100 T2 EP 0783470 A1 SG 66235 A1	08-11-1994 08-02-1996 20-08-1998 22-02-1996 11-11-1999 20-01-2000 16-07-1997 20-07-1999
WO 0015736	A	23-03-2000	US 6332974 B1 AU 5680899 A BR 9913583 A EP 1144551 A2 NO 20011245 A WO 0015736 A2	25-12-2001 03-04-2000 22-05-2001 17-10-2001 10-05-2001 23-03-2000
US 6165949	A	26-12-2000	AU 5690299 A BR 9913410 A EP 1114132 A2 NO 20011123 A US 2002086803 A1 WO 0014188 A2	27-03-2000 22-05-2001 11-07-2001 02-05-2001 04-07-2002 16-03-2000
WO 9721788	A	19-06-1997	AU 1053597 A BR 9611898 A CA 2237068 A1 EP 0876446 A1 JP 2000502135 T NO 982629 A TW 442565 B WO 9721788 A1 US 6096940 A ZA 9609890 A	03-07-1997 16-05-2000 19-06-1997 11-11-1998 22-02-2000 08-06-1998 23-06-2001 19-06-1997 01-08-2000 12-06-1997
US 6179994	B1	30-01-2001	AU 5693899 A BR 9913412 A EP 1144552 A2 NO 20011000 A WO 0014184 A2 US 6375830 B1	27-03-2000 22-05-2001 17-10-2001 04-05-2001 16-03-2000 23-04-2002
EP 0776959	A	04-06-1997	EP 0776959 A2 AU 705415 B2 AU 7198896 A CA 2191290 A1 CN 1167811 A JP 9221685 A SG 74001 A1 TW 416981 B ZA 9609906 A	04-06-1997 20-05-1999 05-06-1997 29-05-1997 17-12-1997 26-08-1997 18-07-2000 01-01-2001 28-05-1997
WO 0118156	A	15-03-2001	FR 2798136 A1 AU 7299300 A EP 1212390 A1 WO 0118156 A1	09-03-2001 10-04-2001 12-06-2002 15-03-2001
WO 9920720	A	29-04-1999	AU 739549 B2 AU 1088699 A	18-10-2001 10-05-1999

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/02366

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9920720	A	BG 104433 A	31-01-2001
		BR 9813120 A	15-08-2000
		CA 2306886 A1	29-04-1999
		CN 1279708 T	10-01-2001
		EP 1029029 A1	23-08-2000
		HR 20000259 A1	31-12-2000
		HU 0100005 A2	28-05-2001
		JP 2001520302 T	30-10-2001
		NO 20002010 A	14-06-2000
		PL 340097 A1	15-01-2001
		SI 20333 A	28-02-2001
		SK 5802000 A3	11-06-2001
		TR 200001084 T2	21-09-2000
		WO 9920720 A1	29-04-1999
		US 6090989 A	18-07-2000
		ZA 9809526 A	19-04-2000

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)